

# Lessons 1&2

## Introduction

Surface science = analog to bulk solid state science. In some cases I will give “refresher” lectures for those not familiar with Solid State Physics.

Textbooks and notes: I will provide notes on each lesson. You can download them from my web page (free).

Other books:

<i>Physics at Surfaces</i>	Zangwill (Cambridge)
<i>Introduction to Solid State Physics</i>	Kittel
<i>Solid State Physics</i>	Ashcroft and Mermin
<i>Surface Science</i>	K. Oura, V.G. Liffshits et al. Springer
<i>Physical Chemistry of Surfaces</i>	Adamson (Wiley)
<i>Intermolecular and Surface Forces</i>	Israelachvili (Academic Press)
<i>Volume 5 of Landau and Lifshitz</i>	
<i>Surface Forces</i>	B.V. Derjaguin, N.V. Churaev and V.M. Muller. Plenum
<i>Statistical Physics of Crystal Growth</i>	Yukio Saito, World Scientific
..... more will be added .....	

## Why and where surfaces are important:

- Frontier of the material, broken chemical bonds or fewer molecules exerting attraction (van der Waals) → this gives rise to an energy per unit area
- Bulk termination structure expected to be different from that expected from the bulk structure
- Semiconductor surfaces give rise to special electronic effects
- Heterogeneous catalysis is a surface enhanced chemistry
- Environmental phenomena: rock weathering, atmospheric phenomena
- Crystal growth
- Nanoscience: Atoms at the surface can be a large % of total.

### Thermodynamics review:

System variables:  $N, V, p, T, S, \mu$

- First principle:  $\bar{\delta}Q = \delta U + \bar{\delta}W$  ( $\bar{\delta}$  symbols meaning non-exact differentials),  $Q$  heat,  $W$  mechanical or other work.
- Second principle:  $\delta S = \frac{\bar{\delta}Q}{T}$  (for reversible processes;  $>$  for irreversible ones)
- Together they lead to the fundamental relation:  $T\delta S = \delta U + p\delta V + \bar{\delta}W$
- Euler equation: From the linearity of  $U$  on extensive variables  $U = \mu N - pV + TS$ , where  $\mu = \partial U / \partial N$ ;  $p = -\partial U / \partial V$ ; and  $T = \partial U / \partial S$ , are the three conjugate variables of  $N, V$  and  $S$ , the normal variables of the energy, as a thermodynamic potential.
- Gibbs-Duheim equation: The differential of Euler eq. together with the fundamental eq. (1), leads to:  $SdT - Vdp + Nd\mu = 0$

### Potentials:

Energy  $U(S, V, N_j)$ :  $dU = TdS - pdV + \mu_j dN_j$   $U = TS - pV + \mu_j N_j$

Helmholtz free energy  $F(T, V, N_j)$ :  $dF = -SdT - pdV + \mu_j dN_j$   $F = U - TS = \mu_j N_j - pV$

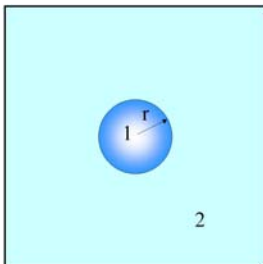
Gibbs free energy  $G(T, p, N_j)$ :  $dG = -SdT + Vdp + \mu_j dN_j$   $G = U - TS + pV = \mu_j N_j$

Omega potential  $\Omega(T, V, \mu_j)$ :  $d\Omega = -SdT - pdV - N_j d\mu_j$   $\Omega = F - G = -pV$

The term  $-pV$  represents the “mechanical energy”. If other forms of mechanical or electrical energy exist they should be added. For example the surface tension  $\gamma$   
 $\gamma = \delta\Omega/\delta A$  or  $= \delta F/\delta A$  depending on the variables that stay constant in the system

### Surface tension

Lets consider two phases 1 and 2, separated by a surface of area  $A$ , in equilibrium. Since  $\mu$  and  $T$  are constant we use the Omega potential:

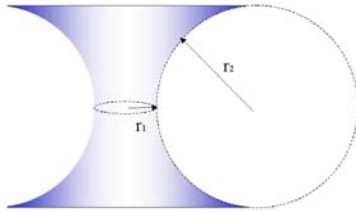


$$\Omega = -p_1 V_1 - p_2 V_2 + \gamma A$$

Where  $\gamma$  is the energy to create a unit of surface. Since  $V_1 + V_2 =$  constant,  $d\Omega = -(p_1 - p_2)dV_1 + \gamma dA = 0$ , in equilibrium. For a planar surface this means  $p_1 = p_2$ , since  $dA = 0$ .

For a spherical droplet or bubble,  $V_1 = 4/3\pi r^3$ , and  $A = 4\pi r^2$ , we

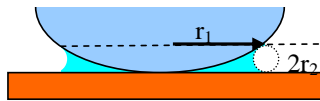
obtain:  $p_1 - p_2 = 2\gamma/r$



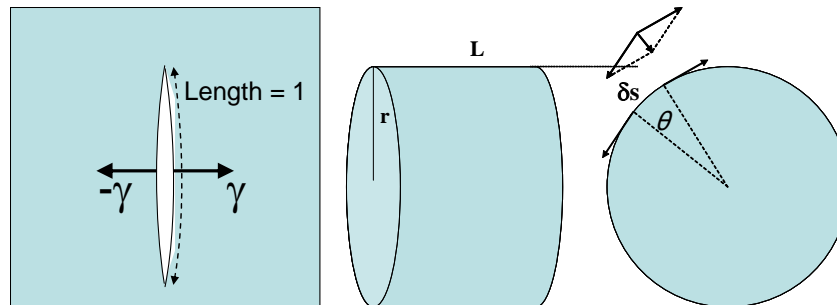
For bubbles  $r < 0$ , and for a liquid filament (figure on the left),  $r_1 > 0$ , and  $r_2 < 0$

$$p_1 - p_2 = \gamma/r_1 - \gamma/r_2$$

*Exercise 1: Calculate the pressure due to capillary condensation at the apex of a sphere (or AFM tip):*



*Exercise 2: Find the geometrical relation between  $\gamma$  and the increase in pressure in the concave side of an interface.*



We can explain  $\Delta p$  as the result of a tangential pull from  $\gamma$  (= force per unit length, left figure) on any line segment on the surface. For a “cut” perpendicular to a principal radius of curvature  $r$ , this produces a force towards the center  $f \sim \gamma \cdot L \cdot \theta = \gamma \cdot L \cdot \delta s / r$ . The increase in pressure is  $f / (\delta s \cdot L) = \gamma / r$ . The same reasoning for the pull on a line segment on the other principal curvature,  $r'$ , will add another term  $\gamma / r'$ .

### Equilibrium gas pressure

The pressures  $p_1$  and  $p_2$  near a curved surface are therefore different from the pressure of the gas over a flat surface, which defines the equilibrium vapor pressure  $p_0$ . Lets calculate the difference between  $p_1$  and  $p_2$  and  $p_0$ .

We start with  $\mu_1(p_1, T) = \mu_2(p_2, T)$  and the relations  $\mu(p, T) = \mu(p_0, T) + kT \log(p/p_0)$ . For the vapor in equilibrium with the flat surface we also have  $\mu_1(p_0, T) = \mu_2(p_0, T)$ . Combining we get:

$$\mu_1(p_1, T) - \mu_1(p_0, T) = \mu_2(p_2, T) - \mu_2(p_0, T)$$

and for small differences in pressure, by series expansion and using the equality:  $v = -\partial\mu/\partial p$ , we get:

$$v_1 \delta p_1 = v_2 \delta p_2,$$

where  $\delta p_j \equiv p_j - p_0$ . Since  $\delta p_1 - \delta p_2 = 2\gamma/r$ , substituting we obtain:

$$\delta p_1 = \frac{2\gamma}{r} \cdot \frac{v_2}{v_2 - v_1} \approx \frac{2\gamma}{r}, \text{ and, since } v_2 \gg v_1, \delta p_2 = \frac{2\gamma}{r} \cdot \frac{v_1}{v_2 - v_1} \approx \frac{2\gamma}{r} \cdot \frac{v_1}{v_2}$$

Using the perfect gas equation:  $pV = NkT$ , we have  $v_2 = kT/p_2 \sim kT/p_0$ , so:

$$\delta p_{vap} = \frac{2\gamma v_{liq} p_0}{rkT}$$

which gives the increase in vapor pressure over a spherical droplet, relative to that on the flat surface. Therefore, if there is a collection of droplets, there can be no equilibrium. The big ones will grow at the expense of the small ones, since these would require higher vapor pressure around them. This is the so called **Ostwald ripening**.

For very small droplets, we cannot use the approximation  $v_1 \delta p_1 = v_2 \delta p_2$ , since  $\delta p_2$  can become quite large. We then need to use the unexpanded form of  $\mu(p, T) = \mu(p_0, T) + kT \log(p/p_0)$  for the gas phase. With this we get:

$$\log \frac{p_{vapor}}{p_0} = \frac{2\gamma v_{liq}}{rkT}$$

*Exercise 3: Find  $p_{vapor}$  for water ( $\gamma = 73 \text{ mJ/m}^2$ ) for droplets of radius 1000, 100, 10 Å.*

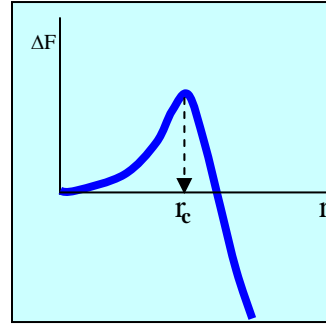
For 100 Å the increase is 10%, and if  $r = 10 \text{ Å}$ , it increases by a factor 2.7! That is why condensation will not occur even if equilibrium dictates it should (supercooling). This is the problem of nucleation.

## Nucleation

Let's consider now the energy cost of nucleating a drop (or bubble) out of equilibrium, ( $\mu_1 \neq \mu_2$ ). The free energy will increase by the amount:

$$\Delta F = \Delta\Omega + \Delta\mu N = \gamma A + (\mu_1 - \mu_2)N = 4\pi r^2 \gamma + (\mu_1 - \mu_2) \frac{4}{3}\pi r^3 / v_{\text{liq}}$$

If  $\mu_1 > \mu_2$ , then of course no condensation can occur. If the vapor is supersaturated, then  $\mu_1 < \mu_2$ , and the cubic term is negative. The graph looks like the one in the figure.



A density fluctuation must generate a nucleus of radius larger than  $r_c$  to nucleate a drop. Differentiating we find:

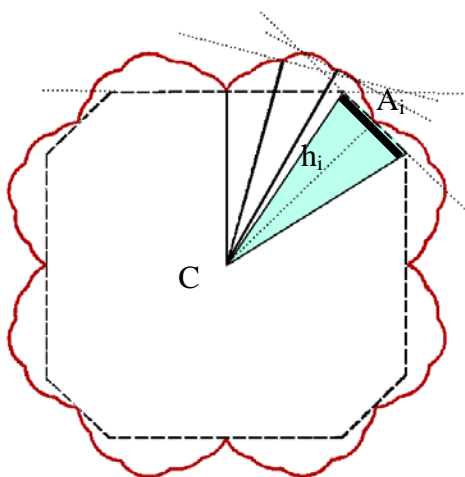
$$r_c = 2\gamma v_{\text{liq}} / (\mu_2 - \mu_1)$$

and the barrier calculated from this is:  $\Delta F = \frac{4}{3}\pi r_c^2 \gamma$

*Exercise: Calculate  $r_c$  for water ( $\gamma = 73 \text{ mJ/m}^2$ ) if  $\Delta F = kT_{RT} = 4.1 \times 10^{-21} \text{ J}$ . What can we conclude from the applicability of the theory?*

The result is  $r_c = 1 \text{ \AA}$  !!! This shows that one cannot push too much the calculations using continuum mechanics concepts, like a spherical form etc.

### Equilibrium shape of crystals: Wulf's theorem



Unlike in the liquid materials we have been studying till now, the surface tension of crystalline solid materials, depend on the atomic arrangement at the surface, which depends on the orientation, i.e., on the surface Miller indices (to be described later). For that reason the equilibrium shape of a crystal as it solidifies from a liquid drop, changes from spherical to polyhedral. Intuitively one expects low surface tension orientations to be predominant. This will undoubtedly include the most compact surfaces, i.e., with low

Miller index, since there the number of broken bonds is minimal. The first treatment of the problem was by Wulf in 1901. Here is his theorem:

Consider a crystal polyhedron (broken lines in the figure) delimited by surfaces  $A_i$ , in equilibrium with its vapor. These surfaces are at a distance  $h_i$  from the center  $C$ . Large surfaces are closer to the center than smaller ones, as shown in the figure.

In equilibrium we must have:  $\delta\Omega = -p_s\delta V_s - p_v\delta V_v + \sum_i \gamma_i \delta A_i = 0$

The conditions are: total volume constant:  $V = V_s + V_v$

same chemical potential:  $\mu_s = \mu_v$

uniform temperature:  $T = \text{constant}$

The crystal volume is:  $V_s = \sum_i \frac{1}{3} A_i h_i$  so that  $\delta V_s = \frac{1}{3} \sum_i [h_i \delta A_i + A_i \delta h_i]$

From the figure we see also that  $\delta V_{s,i} = A_i \delta h_i = \frac{1}{3} (h_i \delta A_i + A_i \delta h_i) = \frac{1}{2} (h_i \delta A_i)$ .

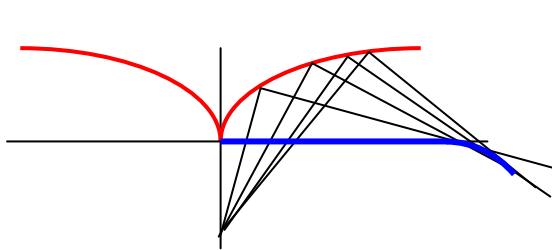
Substituting into  $\delta\Omega$ , with  $\delta V_s = -\delta V_v$ , we get finally

$$\sum_i \left\{ \frac{1}{2} (-p_s + p_v) h_i + \gamma_i \right\} \delta A_i = 0$$

This should be true for any value of  $\delta A_i$  (they are independent variables). Therefore,

$$\gamma_i / h_i = \text{constant}$$

This is Wulff's theorem. It implies that the areas of the facets exposed by the crystal can be obtained by tracing radii in the appropriate direction with a length proportional to  $\gamma_i$



and a plane perpendicular to the radius vector. The minimal polyhedron delimited by the intersection of the innermost planes is the equilibrium shape.

Although the construction in the previous figure shows flat surfaces delimiting the crystal polyhedron, it is not obvious that the flat facet under a sharp cusp (a low Miller index plane) should be delimited by other flat facets, as indicated in the drawing. In fact the envelope of tangents can be curved.

The shape of  $\gamma(\mathbf{n})$  changes from spherical, when the crystal is liquid (melted) to one with cusps at the positions of the most stable surfaces, which are the **low Miller**

**index planes.** In these surfaces the atoms lose the least amount of bonds by the truncation of the crystal. For example, in an fcc or hcp crystal, the coordination goes from 12 in the bulk to 9 in the (111) surface, and to 8 in the (100) surfaces. The formation of singularities or cusps is due to the discrete nature of matter, so that when the orientation changes steps are formed. The interaction between steps determines the nature of the cusp. If  $E_s$  is the energy per unit length step, and if  $\theta$  is the angle away from the singular surface, the density of steps is  $1/a \cdot \tan(\theta)$ , where  $a$  is the step height. The extra surface energy per u. area ( $\gamma$ ) is then:

$$\gamma = E_s \cdot 1/a \cdot |\theta| \quad (\text{for small } \theta\text{'s}).$$

So that:

$$\gamma(\theta) = \gamma(0) + E_s \cdot 1/a \cdot |\theta|$$

This represents a cone in a  $\gamma(\theta)$  plot. The cone needs not be symmetric because the value of  $E_s$  might be different for  $\theta > 0$  than for  $\theta < 0$  as the step orientation changes.

Advanced topic: ON THE STABILITY OF STRUCTURE OF CRYSTAL SURFACES. [See N. Cabrera paper or my notes in Surf. Sci. Course]

### low-index surfaces

